

PART I.
THE REDUCTION POTENTIALS OF SOME
INORGANIC COORDINATION COMPOUNDS

BY
JAMES VINCENT QUAGLIANO

B. S., Polytechnic Institute of Brooklyn, 1938

M. S., Polytechnic Institute of Brooklyn, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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PART I

THE REDUCTION POTENTIALS OF SOME INORGANIC COORDINATION COMPOUNDS

INTRODUCTION

The purpose of this investigation was to make a quantitative study of the reactions that take place at the dropping mercury electrode when a solution of hexammine cobaltic ion is electrolyzed in the presence of a large excess of various inert salts, and establish the conditions under which the reduction of this ion is reversible. Half-wave potentials of oxidation-reduction reactions obtained at reversible conditions have, over those which are irreversible, the great advantage of a thermodynamic significance which can be related to the ordinary standard potentials. Furthermore, the quantitative measurements can be applied advantageously to the study of the strength of the bonds between the central atom and the coordinating molecules, to the determination of diffusion coefficients of complex ions (and molecules), to obtain information about optimum conditions in the preparative work of inorganic complexes, and to the study of inorganic systems that can not be studied by classical methods.

PREVIOUS INVESTIGATIONS

Most of the complex ions which have been studied by the polarographic method were prepared by the addition of the metallic ion to a large excess of the complex forming substance, which also acted as the supporting electrolyte. Brdicka (1) found that the hexammine cobaltous ion is oxidized by dissolved oxygen in ammonical solutions and the resulting hexammine cobaltic ion produces a double polarographic wave. The analysis of solutions prepared by dissolving pure complex cobaltic salts was made recently (2, 3).

APPARATUS AND EXPERIMENTAL METHODS

The principle of the method of determining the half-wave potentials is illustrated by the following description of some preliminary experiments. Purified hydrogen gas was passed into the electrolysis cell (containing the solution to be analyzed) for about twenty minutes to displace all of the dissolved oxygen, at which time the flow was discontinued. The potential of the dropping mercury electrode was increased in increments of 0.05 volt, and the amperage reading was recorded from a Fisher Electropode.

EXPERIMENTAL RESULTS

The effect of gelatin and octyl alcohol in the reduction of the hexammine cobaltic ion at the dropping electrode are very interesting for they not only eliminate the incipient maximum but also displace the wave to more negative potentials. The presence of agar from concentrations of 1.9×10^{-5} to 1.4×10^{-4} per cent produce no change in the half-wave potential of the hexammine ion.

The half-wave potentials and the diffusion currents of the hexammine cobaltic ion were obtained in the presence of six different supporting electrolytes. The half-wave potentials are less negative in solutions of the "indifferent" electrolytes which have little (or no) tendency to coordinate (viz., nitrate and perchlorate). The half-wave potential in the presence of acetate ions is shifted to a more negative value by 0.1 volt, and that in the presence of sulfate ions is more negative by 0.2 volt. A 0.002 per cent solution was found to be the minimal concentration of sodium methyl red which would suppress the maximum.

DISCUSSION

The displaced curves rise more steeply in the solutions which contain the gelatin, and gelatin and octyl alcohol. The adsorbed gelatin and octyl alcohol cause the potential drop to occur in a very small region of solution near the mercury surface. If the potential fall nearly all occurs in the adsorbed

layer, no deformation of ions can occur. Normally, the central atom (Co) is attracted by the electrode, and distortion of the reducible ion (hexammine cobaltic) occurs whereby the central ion is attracted toward the electrode and the coordinating groups (NH_3) distorted away from the electrode, but this is determined by the potential gradient in the solution. In the presence of gelatin a higher potential is necessary.

Although a negative slope in the diffusion current does not occur in the decomposition curve of the hexammine cobaltic ion in the presence of sulfate ions, the presence of a trace (0.002 per cent) of sodium methyl red decreases the diffusion current. This indicates that a new type of maximum behavior takes place in complex cobaltic solutions, namely, that the stirring effect in the solution at the region of the mercury drop which accompanies the maxima continues with increasing applied potentials.

In the polarographic experiments the concentrations of the indifferent electrolytes are at least one-hundred times that of the ion undergoing reduction. Most likely the anions of the supporting electrolyte are bound by ionic bonds in a second sphere about the hexammine cobaltic ion.

SUMMARY

1. The polarographic reduction of the hexammine cobaltic ion in the presence of chloride, nitrate, perchlorate, acetate, and sulfate ions and ammonia has been studied in the range of -0.05 to -0.8 volt.
2. Capillary active substances such as gelatin and octyl alcohol markedly shift the half wave potentials of the hexammine cobaltic ion to more negative potentials. In the presence of these substances a stirring effect which accompanies the maximum continues with increasing applied potentials.
3. The polarographic analysis of the hexammine cobaltic ion can be made in the presence of methyl red to suppress the maximum.

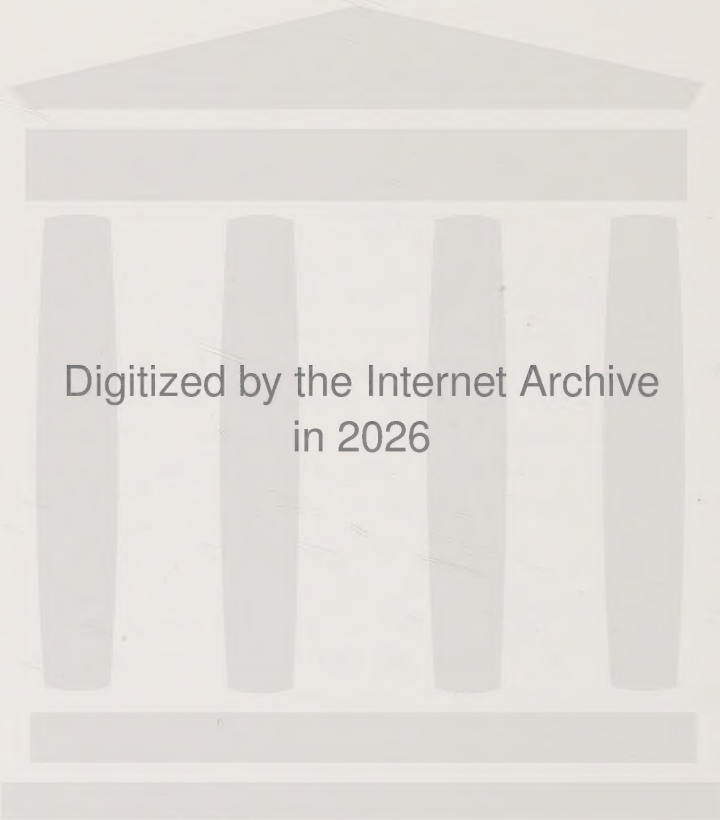
4. The hexammine cobaltic ion is present as the central ion of the super complex in the media of chloride, nitrate, perchlorate, acetate and sulfate ions. In the presence of sulfate and acetate ions, in contrast to the other media, fairly stable "super-complexes" are formed which results in shifting the half-wave potentials to more negative values, and to lowering the diffusion currents.

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VITA

The author was born in Brooklyn, New York, on November 9, 1915. He received his elementary and high school education in the Public Schools of New York City. In 1938 he received the Bachelor of Science degree from the Polytechnic Institute of Brooklyn, and in 1940, the degree of Master of Science. The same year he was appointed instructor of chemistry at Villanova College, a position which he held for three years. In 1943 the author came to the University of Illinois as an instructor in the Army Specialized Training Program, while continuing his graduate studies. The following year he was transferred to an N. D. R. C. Program. During the fall semester in 1945, the author held a University Fellowship.



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